

1994 Annual Report

RESEARCH AND DEVELOPMENT

**Analytical Laboratory Services
Ontario Ministry of Environment & Energy**

March, 1995

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RESEARCH AND DEVELOPMENT
ANALYTICAL LABORATORY SERVICES
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OVERVIEW

Research and Development is an important component of the Ontario Ministry of Environment and Energy (MOEE) analytical laboratory services mandate to provide expert consultation and reference capabilities for environmental analysis. This year's R&D Report represents a further evolution in the reporting of the ministry's analytical research activities. The nature of the individual reports of analytical research studies has changed little from the format used last year. However, the collaborative studies with external groups are reported here for the first time in a separate section. Also, the report includes research performed by Regional laboratory staff, in addition to work done at the Laboratory Services Branch. Thus, this year's R&D report reflects the work performed in the MOEE laboratory system, and not just from one centre.

The amount of collaborative work performed by MOEE analytical laboratory staff is increasing. This reflects the need to conserve resources, and to involve expertise from external organizations where collaboration is mutually beneficial. As such cooperation permits a much greater range of expertise to tackle difficult problems, these collaborations ultimately result in significant benefits to the research itself. More rapid solution of problems, higher quality, and broader scope of application of results are some of the benefits received by university, industry, and government partners.

For further information on any of the projects described in this report, readers are directed to the Author:

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New Applications of Technology

Introduction

The evaluation, application, and adoption of technologies for improved environmental analysis is an ongoing activity. In 1994, the Analytical Laboratory Community of the Ontario Ministry of the Environment and Energy (MOEE) was involved with several projects in which the principal focus was to evaluate novel applications of technologies. Sample preparation technologies such as microwave digestion and solid-phase extraction were examined. A variety of mass spectrometer-based (MS) technologies were also developed, including liquid chromatography-MS (LC-MS), LC-Inductively Coupled Plasma/MS (LC-ICP/MS), negative ion chemical ionization MS (NICIMS), and Ion Trap MS (ITD).

The general thrust in the above development is to provide our customers with improved analytical services, such as lower detection limits, greater specificity, faster turnaround and reduced cost. An additional important in-house concern is to adopt "greener" methods, i.e. - ones that require reduced dependence on toxic organic solvents and mineral acids for extractions and digestions.

The projects described here are not fundamental investigations into the nature of instrumentation systems, nor are they designed to develop new hardware for application to environmental analysis in the remote future. These projects are ones for which the basic technology used is available commercially, but where the specific application development depends more on the technology used than other aspects of the methodology.

I. Microwave Digestion Technique for Trace Metals Analysis of Vegetation, Soil, and Sediment

Study Leader: Liz Pastorek
Study Team: Jane Thrush
Customer:

Objectives

Primary objectives were to:

- ☐ perform metals preparation of soil and vegetation matrices to produce results to within +/- 20 % of initial agreement of present method results;
- ☐ ensure no carryover or contamination of samples;
- ☐ preserve the present detection limits;
- ☐ improve throughput time at the preparation stage;

Background

Historically, the MOEE lab has carried out its vegetation, soil, and sediment metals sample preparation using a strong mixed acid heated digestion. This tends to be labour intensive, time consuming and potentially unsafe. The latest developments in the sample preparation area have included various microwave techniques. One of these, the high pressure vessel microwave system, while relatively fast is still labour intensive. Flow-through systems are being developed that could save staff time while matching the present methods in extraction capability.

As an initial step a flow-through system, from CEM, was brought in for evaluation.

Results

A second study, this time of the Questron System, was carried out. In addition to the basic advantages as shown in the study of the CEM System, the Questron has the advantage of an automatic predigestion of samples if needed. Results using the Questron system matched those obtained by using the present MOEE method very well.

Current Status

A system, CEM or Questron will be purchased, based on the evaluations conducted. At that time detailed optimization studies will be performed, followed by method validation by parallel testing with the present method. This will start once the system is installed, expectedly in May or June, 1995.

II. Negative Ion Chemical Ionization (NICI) Confirmation of Halogenated Organics

Study Leader: Don Robinson
Study Team: Vince Taguchi, Kim Ngo, Bob Kleins
Customer: Mass Spectrometry Laboratory

Objective

To improve Branch capability to identify unknown organic compounds.

Background

Analytical techniques based on the use of gas chromatography/mass spectrometry (GC/MS) instrumentation are considered to be state-of-the-art for the determination of trace organic compounds in environmental samples. These systems work by converting organic molecules into a series of ions, based on the structure of the molecule. The pattern and relative abundances of the ions formed are characteristic of the specific molecule, like a fingerprint.

Negative ions can also be formed, but for various reasons their use has been somewhat limited. One of the major drawbacks of using negative ions is that standard patterns (mass spectra) of these ions are not available for many compounds. To create a library of negative ion mass spectra would help identify unknown organic compounds by providing supplemental information to that obtained by examining positive ion mass spectra.

Results

Negative Ion Chemical Ionization (NICI) was set up on the Finnigan 4500 GC/MS systems and an NICI library of 90 compounds was created. Confirmation of toxaphenes and PCBs have been done in fish extracts.

Current Status

NICI spectra are dependent upon ion source design and instrumental conditions. Because the Finnigan 4500s are being retired and the work is being transferred to the VG Trio-2, the standards previously run on the Finnigan instruments must be rerun on the VG Trio-2. In addition, quantitation of toxaphenes by NICI will be investigated.

III. LC/MS Analysis of Environmental Samples

Study Leader:	Vince Taguchi
Study Team:	Kim Ngo, Dave Wang
Customer:	Mass Spectrometry Unit

Objectives

To expand Branch capability for the determination of thermally-labile compounds, and to identify unknown organic compounds.

Results

Particle Beam (PB) LC/MS has proven to be difficult to reproduce on a daily basis. While the reproducibility problems are being solved, work has begun on sample preparation and quantitation by diode array UV with confirmation by LC/MS.

N-nitrosodiphenylamine (NDPhA) has been recovered from water samples using Ambersorb 572. Quantitation has been done via an external standard with UV detection. There are reproducibility problems with the current protocol. Silanized glassware may be required.

Preliminary work has been done on the analysis of carbamates. This analysis is presently being done by the Pesticides/Herbicides Unit by LC/UV using 4.6 mm i.d. columns. Reverse phase 4.6 mm i.d. columns can accommodate an injection of 100% organic solvent but the 2 mm i.d. columns necessary for PB LC/MS cannot. Therefore, standards and sample extracts must be made up in the exact mobile phase composition selected at the beginning of the gradient.

No work was done on characterization by normal phase LC/MS.

Current Status

The analysis of NDPhA by LC/UV with confirmation by isotope dilution LC/MS, and the analysis of carbamates by LC/UV with confirmation by LC/MS, will be investigated. These compounds will be tested with Electrospray LC/MS when the VG ZAB-EQ is on line. These analyses may be transferred from Particle Beam to Electrospray LC/MS if the latter technique proves to be more reproducible.

IV. Evaluation of Ion Trap Mass Spectrometry Detector (ITD) for Organics in Drinking Water

Study Leader:	Patrick Crozier
Customer:	LSB: Improved Quality and Reliability for the Determination of Organics in Drinking Water

Objective

To evaluate a GC/ITD instrument system, and to determine the applicability of the system to the target compound analysis of pesticides and herbicides in drinking water and related sample types.

Background

The ion trap mass spectrometry detector (ITD) is not a new instrument, but the recent developments have made GC/ITD hardware much more reliable for routine use. The sensitivity of the detector, spectral information provided and its general applicability make it ideal for organic compound environmental testing.

The Laboratory Services Branch is continually testing new equipment and methods in order to improve laboratory performance in the areas of data quality and client services (increased through-put, decreased through-put times, etc.). Several instrument developments have taken place in the area of organic compound analyses. Mass spectrometry is becoming much more important in environmental analysis. If routine target compound analytical methods can be developed which incorporate mass spectrometry, then rapid, quality results can be produced which not only give the analyst accurate sample concentrations but also compound confirmation simultaneously. These types of results are especially important in the area of potable water analysis where human health is a priority.

Results

The GC/ITD software system is fast, easy to use and very flexible. Library searches are done in seconds and the movement between software applications almost instantaneous.

Almost all target compounds analyzed in the Pesticides/Herbicides Unit can be analyzed using the GC/ITD system equipped with a solvent programmable injector (SPI), including target analytes presently analyzed by HPLC. Current method detection limits can be achieved for greater than 95% of target compounds. Since compound sensitivity can be achieved in full scan mode, several current analytical scans (eg. triazine herbicides, organophosphorus pesticides and PAHs) can be combined into one analysis. NIST library matches on target compound spectral data exceeded 80% and did not tend to vary with compound concentrations used in the evaluation. It is suggested that in-house libraries be created if routine target compound methods are developed.

Within-run instrument accuracy and precision results, generated from eight injections of a 41 compound standard mixture, were excellent. The 41 compound standard mixture contained target compounds from triazine herbicides (LSB Method E3121A), organophosphorus pesticides (LSB Method E3224A) and polynuclear aromatic hydrocarbon (LSB Method E3086A) methods. Quantification results ranged from 96.7% to 107.1% with most of the results being close to 100%. Relative standard deviations were between 0.0% and 5.4% with the vast majority of the RSD's being approximately 2.0%. Instrument linearity was demonstrated over a minimum of two orders of magnitude with least square fit correlation coefficients for all compounds exceeding 0.995.

The ion trap automatic gain control (AGC) seemed to handle co-eluting compounds of differing concentration reasonably well. The quantification of and instrument sensitivity to co-eluting triazine and organophosphorus compounds, differing in concentration by two orders of magnitude, was affected only minimally.

Current Status

The only true test of the GC/ITD system is to develop a routine GC/ITD analytical method and monitor instrument performance on real matrix samples over an extended period of time. Staff time and the lack of an available GC/ITD system preclude this evaluation at the present time.

Publications and Presentations

1. Evaluation Report of Varian Saturn™ GC/ITD System Using PHU Target

Compounds - Sensitivity, Spectral Quality and Library Matching : LSB-DWA Internal Report by P. Crozier.

2. Supplemental Evaluation of Varian Saturn™ II GC/ITD System Using PHU Target Compounds - Accuracy, Precision, Interferences and Compound Co-elution: LSB-DWA Internal Report by P. Crozier.
3. Drinking Water Analyses Section Pesticides/Herbicides Unit Target Analyte Listings - Mass Spectra and Structures - February 1994 : LSB-DWA Internal Document by P. Crozier.
4. C. Jennison; J. Jennison. *Rapid Simultaneous Quantitation of Triazines, Organophosphates and PAHs*. Varian GC/MS Application Note, Number 35, October 1994.

Methods Development

Introduction

Much of the method development research performed by Analytical Laboratory Services is in response to customer requests to monitor new environmental contaminants or to expand the scope of specific methods to different sample types. Research objectives commonly include improving the ruggedness of methods, achieving lower detection limits, increasing sample throughput and reducing cost, increasing the degree of automation, reducing the use of toxic solvents, and generally improving the quality of analytical data including precision, accuracy, and freedom from interferences.

Methodology enhancements that address the above considerations are an ongoing activity of any modern analytical laboratory. These activities are essential to maintain reference capabilities and services that can be used to ensure a province-wide analytical laboratory system that delivers readily available and acceptable quality testing. A large range of enhancements to methods are investigated, from simple adjustments to sample extraction times, to major changes such as the use of a completely different detection system. In this report are listed the major studies.

I. Development of Analysis Protocols for Compost Materials

Study Leader: Liz Pastorek
Study Team: Esa Mistry; Sasan Bina; Darryl Russell
Customer: Waste Reduction Branch

Objectives

The objectives are:

- ☐ to establish method performance criteria for metals, Arsenic, and Mercury;
- ☐ to evaluate sample processing, especially the effects of particle size on results;
- ☐ to develop MOEE methods.

The work will result in a document "A Guide to Sampling and Analytical Procedures for Aerobic Compost in Ontario".

Background

MOEE developed interim Guidelines for compost in November, 1991. Currently there are no analytical methods specified to support the guidelines. Private laboratories are using a variety of methods to perform compost analyses. There is a concern that the analytical data generated by these laboratories may not be comparable or of good quality.

Results

A literature search has been carried out to determine methods already in use. Certified Reference Materials have been acquired to be used to develop performance criteria, (precision, recovery, MDLs). Contact has been established with University of Guelph, which will be involved with sampling.

Current Status

Existing methods for compost, soil, and vegetation will be applied to Certified

Reference Materials to establish performance criteria. The effects of sample processing on analytical results will be evaluated using different sample particle sizes. A MOEE compost method will be developed. The method will be validated by analysis of compost samples.

II. GC/MS Analysis of PAH in Drinking Waters

Study Leader:	P. Crozier
Study Team:	L. Matchuk
Customer:	All Drinking/Surface Water Clients

Objectives

To develop a GC/MS-based method for PAH in drinking water to provide improved quality control, faster analysis time, increased analytical capacity, and reduced use of hazardous solvents for sample preparation.

Background

Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. The carcinogenic nature of some PAHs has elicited their inclusion in environmental control legislation. In drinking waters the World Health Organization (WHO) has recommended the maximum permissible concentration for six representative PAHs (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene) not to collectively exceed 200 ng/L. The Ontario Ministry of Environment and Energy has established the maximum acceptable drinking water guideline for benzo(a)pyrene itself to be 10 ng/L.

Results

A routine GC/MSD instrument analysis method has been developed to test for 17 PAHs target compounds. The instrument system is operated in selected ion monitoring (SIM) mode with the analytical run taking 35 minutes. A multi-ramp oven program and sequenced selected ion monitoring is used.

Current Status

A routine wet chemical preparation scheme, suitable for GC/MSD analyses, which incorporates labelled surrogates to monitor sample preparation performance will be developed. Standards verification, method accuracy/precision determination, and comparison with the current HPLC/fluorescence method (LSB Method E3086A) is to be completed after the wet chemical preparation regime is established.

Publications and Presentations

1. Evaluation of the Hewlett Packard 5971E MSD Detector - Benzo(a)pyrene Sensitivity : LSB-DWA Internal Report by S. Jenkins and D. Wang

III. Expansion of Drinking Water Analyses Capabilities

Study Leader:	R. Sadana
Study Team:	L. Grey, J. Mazur
Customer:	Environmental Monitoring and Reporting Branch

Objectives

To develop routine analytical methods to test for additional organic target compounds in drinking water.

Background

The Ontario Ministry of Environment and Energy (MOEE) has revised the Ontario Drinking Water Objectives (MOEE: ISBN # 0-7743-8985-0). The new Ontario Drinking Water Objectives have been expanded from 17 semi-volatile organic target compounds to 50 semi-volatile organic pesticides/industrial chemicals. Originally, LSB did not have the analytical capability to analyze for 18 of these 50 target chemicals. The following is a listing of the compounds initially not analyzed by LSB

but which appear in the new Ontario Drinking Water Objectives:

'Ontario Drinking Water Objectives' Semi-Volatile Organic Compounds <u>not</u> on LSB Drinking Water Analyses Target Compound Lists		
Aldicarb	Diquat	Terbufos
Azinphos-methyl (guthion)	Glyphosate	2,3,4,6- Tetrachlorophenol *
Bendiocarb	Nitrilotriacetic acid (NTA)	Triallate
Bromoxynil *	Paraquat	Trifluralin *
Diclofop-methyl *	Picloram *	Dinoseb
Dimethoate	Temephos	2,4-Dichlorophenol *

* Target Compounds brought on line in 1994

Results

Trifluralin has been added to the current chlorinated organic pesticides/PCBs method (LSB Method E3120B) so that the method now includes 36 target compounds.

Compound	"W" Value ng/L	"T" Value ng/L	Method E3120B	
			% Recovery	% RSD
trifluralin	5	50	112	11

The current chlorophenols/phenoxyacid herbicides method (LSB Method E3119A) has been modified to include five new target compounds. The method now encompasses 16 target compounds. Samples (200 mL) are made acidic ($\text{pH} \leq 1$) with sulphuric acid and passed through pre-conditioned polypropylene C_{18} solid phase extraction (SPE) cartridges. SPE cartridges are then dried and target compounds eluted off the cartridges using a small volume of solvent. The column eluate is treated with diazomethane (to methylate target compounds), evaporated and finally diluted with solvent to 2.5 mL prior to analysis by dual column capillary gas chromatography with electron capture (ECD) detectors. Chlorophenols and phenoxyacid herbicides are quantified as their corresponding methyl esters and

ethers. **Picloram**, **bromoxynil**, **24-DCP**, **2346-TCP** and **diclofop-methyl** have been added to the method.

Compound	"W" Value ng/L	"T" Value ng/L	Method E3119A	
			% Recovery	% RSD
2,4-dichlorophenol	2,000	20,000	76	14
2,3,4,6-tetrachlorophenol	20	200	92	6
bromoxynil	50	500	98	7
picloram	100	1,000	55	15
diclofop-methyl	100	1,000	93	8

Investigations into the analysis of **dimethoate**, **terbufos**, **temephos** and **azinphos-methyl** are underway. Gas chromatography (GC/TSD) and high performance liquid chromatography (HPLC/UV) methods are being evaluated. Initial investigations indicate temephos cannot be analyzed by GC because it is heat labile but with minor sample preservation/preparation changes dimethoate, terbufos and azinphos-methyl can be added to the organophosphorus pesticides GC/TSD method (LSB Method E3224A).

Ion chromatography equipment has been obtained in order to develop a method for the analysis of **Nitrilotriacetic acid (NTA)**. cursory testing shows NTA can be separated from common ions (F^- , Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- , PO_4^{3-}) found in drinking/surface waters and instrument sensitivity is sufficient to test at levels below the Ontario Drinking Water Objective of 0.4 mg/L.

Current Status

The most appropriate analytical method for organophosphorus pesticides will be determined. If a GC/TSD method is chosen, 3 OPs target analytes will be added to the present organophosphorus pesticides method (LSB Method E3224A). If HPLC analysis is deemed most appropriate, a new analytical method will be developed which will include the current 12 organophosphorus target compounds and 4 new target compounds. Instrument and method performance characteristics will be established for the designated method.

Publications and Presentations

1. The Determination of Organochlorine (OCs), Polychlorinated Biphenyls (PCBs) and other Chlorinated Organic Compounds in Water by GC-ECD : MOEE-LSB Method E3120B.
2. The Determination of Chlorophenols (CPs) and Phenoxyacid Herbicides (PAs) in Water by Solid Phase Extraction (SPE) and GC-ECD : MOEE-LSB Method E3119A.
3. Addition of 2,4-DCP, 2,3,4,6-TCP, Bromoxynil, Picloram and Diclofop-methyl to the Current Pesticides/Herbicides Unit Chlorophenol-Phenoxyacid Scan : LSB-DWA Internal Report by L. Grey and J. Mazur.
4. Organophosphorus Pesticides Method Development - Addition of Azinphos-methyl, Dimethoate, Terbufos and Temephos : LSB-DWA Internal Report by L. Grey.

IV. Disinfection By-Products

Study Leader: G. Kanert
Study Team: W. Offenbacher, J. Fracassi
Customer: Environmental Monitoring and Reporting Branch

Objectives

To develop analytical methods for chlorine disinfection by-products that are currently not being monitored in drinking water.

Background

Chlorine is a disinfectant widely used in drinking water treatment plants. Chlorine is highly reactive and combines very quickly with many naturally occurring organic compounds (humic materials) to produce chlorinated organics. The dominant chlorination products are chloroform, trihalomethanes (THMs) and chlorinated aliphatic acids, especially dichloroacetic acid (DCA) and trichloroacetic acid (TCA). Trihalomethanes represent only a small portion of the total halo-organics produced, with the majority of disinfection by-products being non-volatile polar compounds. It has been estimated that under normal drinking water treatment plant regimes the

formation of halo-acetic acids (HAAs) and halo-acetonitriles (HANs) exceeds THM formation by three to five times. Trihalomethanes are routinely determined in drinking water but simple methods for the analysis of ug/L (ppb) concentrations of the non-volatile, highly soluble chlorinated carboxylic acids and acetonitriles do not exist. Determination of halo-acetic acids and halo-acetonitriles in drinking water is important not only from the standpoint of their being present at significant concentrations but also because many of these compounds are suspected or confirmed carcinogens.

Results

Method development on the haloacetic acid analysis has been completed. A number of different extraction techniques have been evaluated (solid phase extraction with resin and ion exchange cartridges) using low level accuracy/precision, ease of operation, and cost effectiveness as criteria. The overall best technique was found to be a liquid/liquid microextraction of 30mL aqueous sample with 3mL methyl-tertiary-butyl-ether and subsequent derivatization with diazomethane prior to GC/ECD analysis. The method is now in the final validation stage which involves the analysis of a large number of field samples, updating documentation, and fulfilling QA/QC requirements.

Current Status

Final method documentation, including addition of QA/QC information. The wet chemistry method development work for this project is completed.

V. The Determination of Geosmin (GEO) and 2-Methylisoborneol (2-MIB) by Isotope Dilution High Resolution Mass Spectrometry:

Study Leader:	Steve Jenkins
Study Team:	Vince Taguchi, Dave Wang, J-P. Palmentier, Kim Ngo, Kim Hong and Pernille Jorgensen
Customer:	Science and Technology Branch, Plant Optimization Section; Regional Water Treatment Plants (Metro, Peel, Durham, York)

Objectives

1. To develop an improved method for Geosmin and 2-Methylisoborneol using the Ambersorb 572 extraction method (previously developed for NDMA), based on isotope-dilution GC/MS;
2. To investigate the need for high resolution mass spectrometry (HRMS).

Background

Geosmin and 2-methylisoborneol are naturally-occurring compounds that are known to cause taste and odour problems in drinking water. They can arise seasonally from the growth and decay of algae or actinomycetes or other biological activity. Because the olfactory senses are very sensitive and threshold odour levels in the range 2-30 ng/L (ppt) have been reported, detection limits at 2 ng/L are required.

A standard method of analysis for GEO and 2-MIB is Closed-Loop Stripping (CLS)(1 L sample) followed by extraction of the trap and GC/MS analysis of the extract. An external standard method of quantitation is used. This method is labour-intensive. A batch of 4 samples plus 2 QC samples would take 4 days to complete.

Results

A new method was developed. The sample size was reduced to 0.5 L so that replicate analyses could be performed on a 1 L sample. Extraction with Ambersorb 572 provided adequate recoveries. The isotope dilution method for quantitation was instituted using a multi-point calibration system analogous to that used for NDMA. Because of chemical interference problems with low resolution mass spectrometry (LRMS), the use of HRMS was mandatory.

A new highly-productive method was developed for the analyses of GEO and 2-MIB. With this method, the seasonal high demand for analyses was accommodated. A publication describing the method development is in preparation. The new method also addresses the stability problem of GEO and 2-MIB in real samples. While these compounds are stable in organic solvents, 40% of GEO and 5% 2-MIB in water samples are lost after 1 day at 20°C. At 5°C, the losses are 6% and 2.5% respectively. To minimize the problems associated with these losses, the samples are spiked with the d₃-labelled internal standards on the day that they are received. Decomposition of the d₃-labelled internal standards should occur at the same rate as the native GEO and 2-MIB.

Analysis of a set of 20 samples, 17 QC samples and a 17-point calibration curve can be completed in 2 days. There has been an 18-fold increase in the sample preparation productivity. Because there is an increase in the number of QC samples and calibration standards, the overall improvement in productivity is a factor of 10.

Current Status

A limited number of samples have been analyzed by the CLS/GC/MS and Ambersorb 572/HRMS methods. Additional comparative studies will continue when samples and resources are available. The development work on this project is completed.

VI. Hexane Micro-Extraction Roller Methodology

Study Leader : P. Crozier
Study Team : I. Albrecht, J. Mazur
Customer: All Drinking/Surface Water Clients

Objective

To develop routine analytical micro-extraction methods for chlorinated organic pesticides and PCBs in drinking water samples.

Background

Two major types of micro-extraction techniques exist. **Solvent micro-extraction** involves the manipulation of extraction conditions in such a manner that compounds of interest can be extracted from water using a minimum amount of organic solvent which can be directly analyzed by gas chromatography. **Solid phase micro-extraction (SPME)** is a recent development which uses a thin liquid phase (film), bonded to the surface of a fused silica fibre, to adsorb compounds of interest from water so that the target compounds can in turn be heat desorbed into a gas chromatograph for analysis. The solvent micro-extraction technique has been successfully applied to several pesticides by the U.S. Environmental Protection Agency (USEPA Method 505). SPME micro-extraction methods are being published more frequently with Dr. Pawliszyn of the University of Waterloo pioneering the field. Recent articles published by Supelco (Supelco Reporter - Vol. 13, No.6, 1994 and Application Note #6, 1994) and papers in Analytical Chemistry (Vol. 66, No. 17, 1994) have dealt with

pesticides analysis using SPME.

Micro-extraction techniques offer a number of advantages over traditional liquid/liquid extraction techniques. Solvent usage is reduced by a factor of 100 in solvent micro-extraction and completely eliminated in SPME. The need for other chemicals, such as sodium sulphate (drying agent) and Florisil™ (column clean-up), are eliminated in both techniques. Sample manipulation is reduced significantly (no evaporation, no drying, no clean-up, etc.) resulting in better method precision. In SPME the total amount of adsorbed compounds is placed in the gas chromatograph for analysis so the sample size required to achieve pg/L or ng/L method detection limits is minimal, usually < 5 mL. Sample analysis time is also reduced significantly.

In the newly developed Drinking Water Analyses Section method, 36 target compounds are extracted from water using small amounts of hexane. The hexane extract is then directly analyzed by dual capillary gas chromatography without further expensive and labour intensive wet chemical processing. The inclusion of a surrogate allows the monitoring of method performance on each individual sample.

Results

A routine chlorinated organic pesticides / PCBs solvent micro-extraction (hexane/roller) method has been developed to replace an existing analytical method (LSB Method E3120B). The new hexane micro-extraction roller method involves the roller extraction of 800 mL of water with two (2) mL of hexane, after the addition of 100 g of sodium chloride (NaCl). The hexane extract is then removed from the water sample and directly analyzed by dual capillary GC/ECD. A surrogate (1,3,5-tribromobenzene) is added to each water sample prior to analyses enabling monitoring of method performance on an individual sample basis. The new method reduces the time for wet chemical preparation by 75% over the current dichloromethane extraction method.

Solvent/water distribution curves and equilibrium times have been established for each target compound. Target compound recoveries have been tested at various spike levels (pg/L to ug/L). Hexane roller micro-extraction method testing has been completed on a wide variety of real matrix spikes, from Great Lakes waters to bog waters. Average recoveries of the 36 individual chlorinated organic pesticides, chlorinated organic industrial chemicals and PCBs tested exceeded 80%. Relative standard deviations (RSDs) were in the order of 2-5%.

A preliminary SPME method has been developed and an evaluation of the method using spiked reagent water is well underway.

Current Status

Final hexane micro-extraction roller method validation against the current dichloromethane extraction method, using actual naturally contaminated groundwaters, is being completed. The development of a SPME micro-extraction method and its comparison to the hexane micro-extraction roller and current dichloromethane extraction methods is to be completed. The comparison of the micro-extraction methods and current dichloromethane extraction method should give statistical information on any potential differences in analytical results which could be method related. A final report and the method write-up/bench procedure is in the process of being completed.

Publications and Presentations

1. The Application of Micro-Extraction Roller Methodology to Trace Level Pesticides Analyses of Drinking Water : presentation at the International Symposium on Chemistry and Biology of Municipal Water Treatment held at CCIW in Burlington on October 28, 1993.
2. Determination of Ultra-Trace Level Organic Pollutants in Drinking Waters by Advanced Wet Chemical Preparation and Instrument Techniques - RAC Project No. PDF #12 : LSB-DWA Internal Report by I. Albrecht.

VII. Methods for Regulation 347 - Waste Derived Fuel

Study Leader:	Rusty Moody
Study Team:	Ray Leger, George Wood, Ram Sadana, Pamela Wee
Customer:	Industrial Hazardous Waste Section

Objective

To develop methods for a variety of contaminants in waste-derived fuel to support MOEE Regulation 347.

Background

Regulation 347 has a section dealing with Waste Derived Fuel. This fuel is burned by small units for heating purposes, generally in garages. The prime concern is the effect on the air quality by burning this waste oil. Owners of these heating

units must obtain a Certificate of Approval (C of A) before burning a batch of oil. The C of A specifies parameters and concentration levels which cannot be exceeded. LSB analysis requests will come from investigations into the burning of oil which has not passed the C of A. These methods are required for LSB to analyze samples received from abatement and enforcement activities of MOEE.

Results

The required methods are for selected metals, total halogens, nitrogen, phosphorus, sulphur, water, bottom sediments and ash. Completed work on the various methods is summarized below:

Selected Metals. Regulation 347 requires analysis of samples for arsenic, lead, chromium and cadmium. The C of A requirements also list iron, barium, zinc, beryllium, manganese, nickel and silver. A method has been developed for metals (except As) by ICP following ashing. The method has been completed. Recoveries for metals using metal salt or organo-metallic spikes have generally exceeded 90%. The method for arsenic involves ignition in a bomb calorimeter followed by analysis by hydride generation. Recovery studies have improved to 98% recovery.

Total Halogens. This method involves ignition in a bomb calorimeter followed by a potentiometric titration with a silver electrode. Rather than titrate directly with silver, we add an excess of silver ions and back titrate with chloride. A draft method has been written. Collection of data for recovery and precision criteria is the next step. The titration step can also be used for analyzing total halogens in cement following dissolution in nitric acid. Comparison with an external lab for total halogens in cement were within 0.1%, so we have confidence in this portion of the method.

Water and Bottom Sediments. A draft method has been written. Modifications to the centrifuge have been completed.

Ash. A draft method has for waste crankcase oil been completed, based on an ASTM method.

Nitrogen. Work on this method has not been initiated.

Heat Content. A draft method has been completed.

Current Status

Remaining work on this project is summarized in the individual method descriptions above. A major sampling project scheduled for February/March 1995 will provide enough samples to complete the CEA/CEC data requirements for method approval.

Partnerships

Introduction

Partnerships for R&D are becoming increasingly important. Cost saving is the principal factor driving this change, but other factors are also important, such as the ability to share unique resources and expertise. This year's report captures for the first time joint projects between Analytical Laboratory Services staff and staff of other organizations.

The partnership can take form in a number of different ways, and these are reflected in the projects described below. For example, a manufacturer may loan state-of-the-art equipment to Analytical Laboratory Staff for evaluation or for a special project. MOEE staff then perform the actual evaluation work, which may include comparing results generated by the new equipment with results from standard MOEE methods. Projects are also performed where MOEE staff analyze R&D samples generated externally, because the partner does not have direct access to our specialized instrumentation. Other government organizations, academia, and industrial organizations are all potential partners. In all cases, the partnership is undertaken because a significant benefit is possible to all of the contributing partners.

I. Determination of Chromium Species in Environmental Samples Using HPLC-DIN-ICP-MS

Study Leader: M.Powell
Partnership: D. Boomer, MOEE
D. Wiederin, Cetac Technologies, Nebraska
Customer: Environmental Monitoring and Reporting Branch

Objective

To demonstrate the range of applicability of the HPLC-DIN-ICP-MS technique for MOEE applications.

Background

Combining HPLC and DIN-ICP-MS will allow separation of Cr(III) and Cr(VI) species in environmental samples for trace elemental analysis. In addition to performing separation, a total chromium determination may also be made in the same measurement. This will allow analysts to compile concentration data as well as to gather information on changes in ratio between Cr(III) and Cr(VI) over time. By doing this, changes in oxidation state can be observed and studies pertaining to chemical stability for a specific environmental matrix may be performed. This will provide valuable information in determining the most appropriate preservative to use for a particular matrix.

Results

The comparison of this technique with the established MOEE MISA method has been carried out. The method is quite sensitive (ppt levels) and is suitable for studies of ultra trace levels in water samples. Although the techniques were comparable, some problems were encountered with samples changing proportions of oxidation state over time. This causes a change in sample stability and hence produces erroneous results.

This problem was discovered by monitoring changes in the ratio of oxidation states over time. A reduction in sample storage time is necessary to reduce the extent of oxidation state change.

Current Status

In general, the work on method development is complete. This technique can be shaped into a Ministry Method for ultra trace analysis of a variety of matrices (pending client requests).

II. Supercritical Fluid Extraction of Soil Samples for PCDDs/PCDFs

Study Leader:	Eric Reiner
Partnership:	Eric Reiner, Dave Waddell, Ray Clement (MOEE), Clayton Babcock, Dionex, Dave Herbert, Lisa Rerup (ASL Ltd.)
Customer:	Analytical Laboratory Services

Objective

To determine whether SFE methods developed by ASL laboratories are suitable for the determination of dioxins/furans in soil and sediment samples.

Background

Supercritical Fluid Extraction (SFE) is a relatively new environmental sample extraction technique that has the advantage of greatly reduced dependence on the use of organic solvents such as toluene and methylene chloride. Studies have shown that SFE methods are very efficient for some applications, and can save time as well as reducing solvent use. However, SFE is not better than conventional extraction methods for all applications.

ASL is using a Dionex SFE instrument to optimize the conditions for the SFE of PAH from soil samples. They were interested in studying the use of SFE for the chlorinated dibenzo-p-dioxins and dibenzofurans, but did not have access to the specialized analytical facilities needed for the analysis of the sample extracts. The MOEE Dioxin laboratory has state-of-the-art analytical capability for the dioxins/furans, but no direct access to SFE equipment, and no experience in SFE method development. To compare SFE extract results with results from conventional solvent extracts, the Dioxin Unit shipped split samples of soils to ASL. One replicate was extracted by using conventional procedures; ASL extracted the other replicate by using SFE, and shipped the extracts back to the Dioxin Laboratory for analysis.

Results

The SFE-extracted samples gave comparable results to the results obtained by using conventional Soxhlet extraction techniques. However, while some SFE-extracted samples appeared to demonstrate higher analyte recovery compared to Soxhlet, a few other samples exhibited lower analyte recovery. Neither the SFE nor the Soxhlet extraction method was clearly superior for all samples tested. With comparable extraction efficiencies, the SFE method is favoured because of the faster extraction, reduced use of toxic solvents, and reduced use of expensive and difficult-to-clean specialty glassware. Reduced glassware use can reduce the possibility of sample cross-contamination.

Dionex has agreed to loan the SFE instrumentation to the Dioxin Unit, so additional comparison studies can be performed. Each separate matrix type (including different soil types) must be tested individually to determine the efficiency of the SFE method. Although the initial capital cost of the SFE instrumentation is much greater than the cost of the Soxhlet extraction method, the long-term cost savings favour the SFE method, because of reduced solvent use.

III. Field Evaluation of a Membrane Filter/Dissolution Method for the Recovery of *Cryptosporidium* Oocysts and *Giardia* Cysts from Potable Water

Study Leader:	Garry Palmateer, Southwestern Region Peter Boleszczuk, Ministry of Health
Partnership:	Dan Van Bakel (MOEE), Shelly Unger (MOEE), Maryann Langridge (MOH)
Customer:	Environmental Monitoring and Reporting Branch

Objectives

The objectives for this project are:

1. To establish the efficacy of the method using spiked water samples,
2. To determine optimum sample volumes providing maximum cyst recovery from waters exhibiting natural turbidities from 0.03 - 3.0 NTU; and,
3. To investigate the effectiveness of pre-filters when employed with high

turbidity waters (>0.3 NTU).

Background

The Ministry of Environment & Energy and the Ministry of Health are evaluating the efficacy of the method of recovery of *Cryptosporidium* oocysts and *Giardia* cysts from spiked potable water. The method was recently developed by Dr. A. Chagla and Dr. J. Aldom of the Ministry of Health in London using in-house spiked water samples. This method is presently undergoing rigorous field testing at water plants across Southwestern Ontario using spiked 500-1000 L water samples.

Results

Initial experiments have indicated that a 1000 L spiked water sample may be filtered by using a 29.3 cm diameter filter with a 1.2 μm pore size. Filters containing the oocysts are dissolved in acetone. Following centrifugation to concentrate the oocysts, the acetone is decanted. The oocysts are then washed by resuspension/centrifugation four times in a water-ethanol solution. The final oocyst pellet is placed on a microscope slide, stained with monoclonal antibodies, and the oocysts are counted. Percent recoveries ranged from 8.5 to 130, with an average recovery of 45.6. This is much better than the EPA/ASTM method recoveries of 2% for similar type samples. The EPA/ASTM method requires 2.5 days analysis time per sample, the new method requires 2 to 4 hours per sample.

Current Status

The field testing is continuing. The variation in the percent recoveries is partially due to variations in the efficiency with which the oocysts are filtered. Turbidity values of the water are poorly related to the percent recovery of the oocysts. Particle sizing and counting is being initiated on all samples to be tested, in order to elucidate the reasons for the variations in percent recoveries. Other physical and water quality parameters are also to be assessed.

IV. Improved Presence-Absence Medium for the Analysis of Treated Drinking Water

Study Leader: Arthur N. Ley
Partnership: Arthur Ley (MOEE)
Saul Wolfe & Raymond Bowers (Queen's University)
John Molloy (New Parteq)

Objectives

The main objectives of this project are:

1. to improve the detection sensitivity of a Presence-Absence medium to increases in acidity from bacterial fermentation of lactose
2. to develop a medium that detects total coliforms and also is confirmatory and specific for *Escherichia coli*
3. to develop a medium that does not require autoclaving and laboratory preparation

Results

A new and improved Presence-Absence (P-A) test has been developed for the detection of total coliforms and the specific detection of *Escherichia coli* in treated drinking water. The new P-A test does not require the preparation and sterilization of medium by laboratory staff. Compared to the current MOEE P-A medium, the new P-A medium formulation has improved detection characteristics for *Aeromonas hydrophila* and specifically identifies *E.coli* beta-glucuronidase activity. A patent application for the new P-A test is in progress.

Current Status

The development work on this project is completed. Additional effort is required to pursue the patent application, and to investigate commercialization opportunities.

V. PLS/IR Analysis of Oils and Greases in Water and Sediment Samples

Collaboration Between: Metro Toronto Works Laboratory and Ministry of Environment and Energy
Partnership: Alnoor Kotadia and Jack Chan (MTW)
Toan Banh and Paul Yang (MOEE)
Customer: MISA Municipal Section, Program Development Branch

Objective

To apply infrared spectroscopy and partial least square analysis to separate and quantify vegetable oils/animal fats, and motor oils. Ultimately, a method for the direct measurement of analytes from water without solvent extraction is desired.

Background

Oil and Grease analysis (O&G) is a simple but expensive procedure. The reasons are two-fold. From the global point of view, the 1992 Montreal Protocols call for the total elimination of ozone depletion materials, e.g., Freon, by 1/1/1995. As the search for a suitable replacement for Freon has been very difficult, DuPont withdrew from this business. MOEE is not affected now as the current LSB O&G method uses methylene chloride as the extracting solvent. In Toronto, because of the limited capability of the current O&G method, STP surcharges on the order of five to eight million dollars are lost.

Results

LSB is providing one FT-IR, PLS analysis software, and the design of the analytical method. Metro Works is providing one technical staff to do the sample preparation and analysis. Metro Works also designs/carries out a field study using the new method to validate all analytical procedures.

1. The method "The Determination of Solvent Extractable Materials of Vegetable/animal Origins and Mineral Origins Using Infrared and Partial Least Square Analysis" was prepared.
2. Procedures, QC data, and results of the above method were presented at the Oil and Grease Analysis Workshop held at WTC on Sept. 21~22, 1994.
3. LSB and Metro Work have been field testing of the above method on the restaurant and laundry sectors. The report is due the end of June 1995.

External Research

Over many years, Analytical Laboratory Services has been very active in the Environmental Research Program (ERP), with respect to the evaluation and promotion of proposals submitted under the analytical methods research area. This year, the active projects funded by MOEE under this program are listed for the first time in this report. The ERP-funded research permits us to take advantage of special skills and experience not otherwise available to Analytical Laboratory Services. Liaison Officers for these projects are Analytical Laboratory Services staff, who ensure that research stays focussed on MOEE objectives, and who promote the technology transfer of research results to practical applications.

External research proposals are principally submitted by university faculty or by private consultants in response to the MOEE document "Environmental Research Priorities". In the 1994 version of this document (ISSN 1192-4675), four analytical research objectives were listed. Three of the projects described below were submitted in response to these objectives. The fourth project (ERP 707G) was unsolicited, but addressed an important Regional abatement issue. These studies were in their early stages at the time of this report; research findings and associated publications will be documented in future editions of this R&D Annual Report.

I. ERP 701G: The Application of Quadrupole Ion Trap Mass Spectrometry to the Development of New Analytical Protocols for Dioxins/Furans

Environmental Research Program Grant: 701G

Principal Investigator:	Prof. Ray March (Trent University)
Liaison Officer:	Roger Mercer, Laboratory Services Branch
Customer:	Dioxin/Furan Section

Objectives

To discover the optimum operating conditions for analyzing dioxins and furans by ion trap mass spectrometry, and to compare results with those found by using other mass spectrometry techniques.

Background

Current MOEE methods for analysis of dioxins/furans require greater mass spectrometric selectivity than can be provided by low resolution mass spectrometers. LSB Dioxin/Furan Unit (DFU) presently uses a high resolution mass spectrometer and a triple quadrupole mass spectrometer for these analyses. These instruments are expensive, complex, difficult to maintain and require highly trained operators. A newly commercialized version of the quadrupole mass filter — the quadrupole ion trap — could potentially attain sufficient selectivity to perform these analyses by operating as a tandem mass spectrometer (MS/MS). The ion trap has the advantages of relatively low cost, reduced mechanical and electronic complexity and simplified operation when compared with high resolution and triple quadrupole mass spectrometers.

This project is a collaboration between Trent University, Varian Associates and MOEE. Professor Ray March of Trent University has an advanced research version of the ion trap, and is investigating optimal ion trap MS/MS conditions with the support of an RAC grant. Varian Associates has loaned an ion trap to LSB/DFU for evaluation purposes. This instrument is being used to test optimised MS/MS conditions, and will be used to determine instrumental and method detection limits and for field sample intercomparisons.

Results

The experimental plan for this research includes the following;

- ☐ Determine MS/MS conditions for maximum production of diagnostic fragment ions from selected precursor ions (i.e. optimal "conversion efficiency") using native (unlabelled) dioxin/furan standard solutions
- ☐ Create instrumental methods to analyze for both native and labelled ions in a single GC run and determine instrumental detection limits using standard solutions; determine the linear working range and between-run variation in relative response factors using standard solutions
- ☐ Explore the use of protracted ion storage times and/or unidirectional ion ejection to improve sensitivity
- ☐ Determine method detection limits for one or more of DFUs standard blank matrices (reagent water, Ottawa sand, cod liver oil, MISA effluent) using ion trap MS/MS
- ☐ Analyze difficult (i.e. interferent containing) field samples using ion trap MS/MS and compare the results with high resolution and triple quadrupole mass spectrometry

Optimum values for the adjustable trap parameters were studied. The first step was to optimize isolation of the precursor ions, which optimized the majority of the trap parameters. Breakdown curves (plots of conversion efficiency versus excitation energy) were determined for the five native furan congener groups in order to optimize conversion efficiency.

Current Status

The optimal MS/MS conditions found for native furans will be tested using native dioxins, and then with labelled dioxins and furans. We will then pursue the remaining items listed above: create an instrumental method incorporating all native and labelled dioxins and furans; measure the instrumental detection limit and linear working range; investigate ion storage and unidirectional ejection; measure method detection limits; compare ion trap MS/MS results with high resolution and triple quadrupole MS/MS results. We anticipate that these items will be completed by the end of 1995.

II. ERP 707G: Analysis of Sulfur-Containing PAH in Ambient Air and in Selected Sources

Environmental Research Program Grant: 707G

Principal Investigator:	Professor Brian McCarry, McMaster University
Liaison Officer:	Dr. Ray Clement, Laboratory Services Branch
Customer:	Regional Abatement Staff

Objectives

Principal objectives are to develop methods for thia-PAH in urban air samples, and to determine source-apportionment criteria based on the PAH profiles observed in various sample types.

Background

The first year of this investigation will be principally devoted to obtaining the "benchmark" analytical data on which the study will be based. New analytical methods based on liquid chromatography/mass spectrometry will be explored. Methods developed will be used in the analysis of field samples in the second year of this research. PAH profiles will be used to differentiate the various sources of thia-PAH detected in ambient air, and a source-apportionment model will be developed.

III. ERP 720G: Automated Counting of Bacterial Colonies

Environmental Research Program Grant: 720G

Principal Investigator:	Professor Colin Mayfield, University of Waterloo
Liaison Officer:	Mr. Garry Horsnell, Laboratory Services Branch
Customer:	Microbiology Unit, Analytical Laboratory Services

Objectives

The objective of this work is to automate the bacterial colony counting process, to improve productivity and precision for this determination.

Background

Automated image analysis technology will be applied to the process of counting bacterial colonies on membrane filters. A Nikon Microanalyst image analysis system with a colour video camera and image capture board will be used to acquire and analyze images of colonies of coliform bacteria on filters. Computer programs to solve problems of colour discrimination of colonies, agglomerated colonies, differing colony sizes and other issues will be developed. Finally, a detailed comparison between manual, automated macro counting, and microcolony counting systems will be performed.

IV. ERP 729C: Development of an Efficient Extraction and Clean-Up Procedure Based on Commercially Available Solid-Phase Cartridges for the Determination of Chlorinated Dioxins and Furans in Biological Tissues

Environmental Research Program Grant: 729C

Principal Investigator:	Dr. K.W.M. Siu, National Research Council
Liaison Officer:	Dr. Eric Reiner
Customer:	Dioxin/Furan Unit

Objectives

The objective is to develop more efficient extraction and clean-up procedures for the determination of chlorinated dioxins and a related group of contaminants, the chlorinated dibenzofurans.

Background

Different extraction methods, especially those that use only non-chlorine-containing solvents, such as acetonitrile and dimethylformamide, will be investigated, in addition to methods based on supercritical fluid extraction. The clean-up procedure will be based on the use of commercially available "Sep-Pak" type cartridges, which eliminates in-house column preparation, assures higher batch-to-batch uniformity, and minimizes volumes of undesirable solvents or chemicals (no sulphuric acid, no strong base, no ether, and greatly reduced use (factor of 10-100 times lower) of chlorinated solvents. The new methods should save enough time in sample preparation to permit a doubling of sample throughput, compared to the time required for conventional dioxin methods.

Publications and Presentations - 1994

Analytical Laboratory Services

A. Publications

1. G.D. Thurston; J.E. Gorczynski, Jr.; J.H. Currie, D. He; K. Ito; J. Hipfner; J. Waldman; P.J. Liroy; M. Lippmann. *The Nature and Origins of Acid Summer Haze Pollution in Metropolitan Toronto, Ontario. Environmental Research*, 1994, 65, 254-270.
2. V.Y. Taguchi; S.W.D. Jenkins; D.T. Wang; J.-P.F.P. Palmentier; E.J. Reiner. *Determination of N-Nitrosodimethylamine by Isotope Dilution, High-resolution Mass Spectrometry. Can. J. Appl. Spectrosc.* 1994, 39(3), 87-93.
3. R.E. Clement; C.J. Koester; L. Grey. *Determination of Dioxins and Furans in Fish. Chapter 5 in Analysis of Contaminants in Edible Aquatic Resources*; J.W. Kiceniuk and S. Ray, Eds., VCH Publishers, 1994, pp.347-377.
4. S. Davies. *Intelligent Software for Chemical Analysis (Book Review). Anal. Chem.* 1994, 66(7), 416A.
5. S.L. Wong; L. Nakamoto; J.F. Wainwright. *Identification of Toxic Metals in Affected in Affected Algal Cells in Assays of Wastewaters. J. Appl. Phycology* 1994, 6, 405-414.
6. A.J. Neary; W.I. Gizyn. *Throughfall and Stemflow Chemistry Under Deciduous and Coniferous Forest Canopies in South-Central Ontario. Can. J. For. Res.* 1994, 24, 1089-1100.
7. D. Boomer; G. Crawford; C.L. Raposo. *The Determination of Organolead in Water by Gas Chromatography Atomic Absorption Spectrophotometry (GC-AAS). Ontario Ministry of the Environment & Energy Report*, 1994.
8. D. Toner; P.W. Crozier; O.W. Berg. *Immunoassay Techniques Environmental Applications. Ontario Ministry of Environment & Energy, Laboratory Services Branch, Internal Report* 1994.
9. S. Janhurst. *Performance Report: Water Quality Analyses Section - 1992. Ontario Ministry of Environment & Energy, Laboratory Services Branch Report*, 1994.
10. S. Janhurst. *Performance Report: Water Quality Analyses Section - 1993. Ontario Ministry of Environment & Energy, Laboratory Services Branch Report*, 1994.

11. S. Cussion. *Polychlorinated Biphenyl (PCB) Isomers in Support of the Integrated Atmospheric Deposition Network (IADN)*. Ontario Ministry of the Environment & Energy, Laboratory Services Branch Report, 1994.
12. B. Jobb; R.B. Hunsinger; O. Meresz; V.Y. Taguchi. *Removal of N-Nitrosodimethylamine from the Ohsweken (Six Nations) Water Supply: Final Report*. Ontario Ministry of Environment & Energy, Science and Technology Branch Report, 1994.
13. B. Jobb; R.B. Hunsinger; O. Meresz; V.Y. Taguchi. *Ultraviolet Degredation of N-Nitrosodimethylamine (NDMA) in the Ohsweken (Six Nations) Water Supply*. Ontario Ministry of Environment & Energy, Science and Technology Branch Report, 1994.
14. R. Bloxam; H. Sahota; S. Davies; G. Minichini. *Windsor Air Quality Study: Mathematical Modelling and Source Apportionment*. Ontario Ministry of Environment & Energy, Science and Technology Branch Report, 1994.

B. Presentations

1. D. Boomer, "Application Development with Commercial Software", Course presented at the ICP Winter Conference, California, U.S.A., January 1994.
2. D. Boomer, "Direct Computer Input Workshop", Workshop presented as part of the Analytical Laboratories Council *Seminar Series*, Toronto, Ontario, April 1994.
3. R.E. Clement, "How to Present a Seminar", Invited Seminar presented to Graduate Students, Chem 501 (Environmental Chemistry), University of Western Ontario, September 29, 1994.
4. R.E. Clement, "The Role of Laboratory Testing in Society", Plenary Lecture presented to 300 high school students, Ontario Science Centre, Toronto, Ontario, October 17, 1994.
5. R.E. Clement, "Dioxins in the Environment: Sources, Distribution, and Analytical Challenges", Invited Lecture presented at the conference on *Environmental Chemistry*, Dalhousie University, Halifax, Nova Scotia, October 22, 1994.



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